

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 028 348
B2

(12)

NEW EUROPEAN PATENT SPECIFICATION

(45) Date of publication of the new patent specification:
16.09.87

(51) Int. Cl.: **C 08 F 220/44, C 08 F 6/00**

(21) Application number: **80106399.1**

(22) Date of filing: **21.10.80**

(54) Treating dispersions of acrylonitrile polymers.

(30) Priority: **26.10.79 US 88439**

(43) Date of publication of application:
13.05.81 Bulletin 81/19

(46) Publication of the grant of the patent:
11.04.84 Bulletin 84/15

(45) Mention of the opposition decision:
16.09.87 Bulletin 87/38

(84) Designated Contracting States:
BE DE FR GB IT NL

(56) References cited:
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Description

Background of the invention

Acrylonitrile is the basis for a family of important commercial polymers. For example, copolymers of butadiene with less than 50% acrylonitrile provide oil resistant polymers. Copolymers of alkyl acrylates with acrylonitrile provide a range of polymer products. For example when ethyl acrylate is the major component oil resistant elastomers are obtained; and when acrylonitrile is the predominant comonomer, useful molded plastic materials are obtained. Copolymers of a major proportion of styrene and minor proportions of acrylonitrile are also useful in modifying vinyl chloride polymers, as moldable plastics and as components of ABS resin blends. Normally these acrylonitrile containing polymers are prepared by polymerization in water. Even when such polymerizations are substantially complete, there still remains undesirable amounts of unpolymerized acrylonitrile dissolved both in the polymer and the water. Normal procedures of stripping by vacuum or steam does not normally remove all of this undesirable acrylonitrile.

Summary of the invention

Residual acrylonitrile dissolved in acrylonitrile homo- or copolymers and/or water in which acrylonitrile polymers are polymerized or processed such as a latex thereof or from acrylonitrile processes can be substantially reduced by adding to polymer-water mixtures, for example, after at least 90% of the monomers have been polymerized, additional catalyst and an amount of comonomer in excess of the amount of free acrylonitrile present.

The aqueous suspensions or dispersions of acrylonitrile polymers used in practicing the present invention are obtained by polymerizing acrylonitrile alone, or more normally with other vinylidene comonomers to form copolymers, for example with 50 weight percent or more of butadiene, up to 50 weight percent acrylonitrile with 50-95 weight percent styrene, and 5-50 weight percent acrylonitrile with: 1-99 weight percent each of an alkyl acrylate such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate with styrene and acrylonitrile on a butadiene polymer in the well-known ABS resins, and other copolymers.

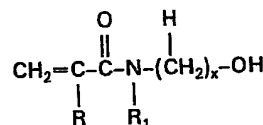
Typically, the polymerizable comonomers used in addition to butadiene and styrene

will be vinylidene monomers having at least one terminal $\text{CH}_2 =$ group. Polymerizable comonomers useful in the present invention include: other vinyl aromatics as α -methyl styrene and chlorostyrene; α -olefins such as ethylene, propylene, and isobutylene;

other α , β -olefinically unsaturated nitriles as methacrylonitrile; alkyl vinyl ethers such as methyl vinyl ether, isopropyl vinyl ether; n-butyl vi-

nyl ether, isopropyl vinyl ether, and haloalkyl vinyl ethers as 2-chloroethyl vinyl ether;

vinyl ketones; vinyl pyridine, α , β -olefinically unsaturated amides such as acrylamide, N-methyl acrylamide, N-t-butyl acrylamide, N-cyclohexyl acrylamide, diacetone acrylamide; methacrylamide, and N-ethyl methacrylamide, α , β -olefinically unsaturated N-alkylol amides having the structural formula



wherein R is a hydrogen or an alkyl group containing from 1 to 4 carbon atoms and x is a number from 1 to 4, R₁ is hydrogen or an alkyl group such as N-methylol acrylamide, N-ethylol acrylamide, N-propylol acrylamide, N-methylol methacrylamide, and N-ethylol methacrylamide; polyfunctional compounds such as methylene-bisacrylamide, ethylene glycol dimethylacrylate, diethylene glycol diacrylate, allyl pentaerythritol and divinyl benzene;

Mixtures of one or more of the above-mentioned monomers may be employed if desired.

Generally, butadiene or alkyl acrylate polymers will contain 50 to 70% by weight butadiene, or alkyl acrylate wherein the alkyl group contains 1 to 8 carbon atoms, 20 to 45% of acrylonitrile and up to about 20% by weight of other polymerizable vinylidene comonomers interpolymerized.

The polymer latices may be prepared using any of the conventional polymerization techniques known to those skilled in the art, usually in an aqueous emulsion. The emulsifier may be charged at the outset of the polymerization or may be added incrementally or by proportioning throughout the run. Any of the general types of anionic, cationic or nonionic emulsifiers may be employed, however, best results are generally obtained when anionic emulsifiers are used. Typical anionic emulsifiers which may be used include those types known to those skilled in the art, for example, as disclosed beginning on page 102 in J. Alphen's «Rubber Chemicals», Elsevier, 1956, for example, the alkali metal or ammonium salts of the sulfates of alcohols containing from 8 to 18 carbon atoms such as, for example, sodium lauryl sulfate; alkali metal and ammonium salts of sulfonated petroleum or paraffin oils; sodium salts or aromatic sulfonic acids such as dodecane-1-sulfonic acid and octadiene-1-sulfonic acid; alkyl aryl sulfonates such as sodium isopropyl benzene sulfonate and sodium dodecyl benzene sulfonate; alkali metal and ammonium salts of sulfonated dicarboxylic acid esters such as sodium dioctyl sulfosuccinate and disodium N-octadecyl sulfosuccinamate; alkali metal or ammonium salts of the free acids of complex organic mono- and diphosphate esters.

So-called nonionic emulsifiers are octyl- or nonylphenyl polyethoxyethanol. Useful as emul-

sifiers are the alkali metal salts of the aromatic sulfonic acids such as sodium salts of the aromatic sulfonic acids and the sodium salts of the alkyl aryl sulfonates of the formula $R-[-Ar-SO_3]-M^+$ wherein R is alkyl or alkenyl having 8 to 20 carbon atoms, Ar is aryl or phenyl or naphthyl and M is the metal ion. In addition to the above-mentioned emulsifiers it may be desirable and advantageous to add postpolymerization emulsifiers and stabilizers to the polymeric anionic latex in order to improve the latex stability if it is to be stored for prolonged periods prior to use. Such post-polymerization emulsifiers may be the same as, or different than, the emulsifier employed in conducting the polymerization but preferably are anionic or non-ionic surface active agents.

To initiate the polymerization free radical catalysts are employed. The use of such catalysts, although in certain systems not absolutely essential, insure a more uniform and controllable polymerization and a satisfactory polymerization rate. Commonly used free radical initiators include the various peroxygen compounds such as the persulfates, organic peroxides, benzoyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide; azo compounds such as azodiisobutyronitrile, and dimethyl azodiisobutyrate. Especially useful as polymerization initiators are the water-soluble peroxygen compounds such as hydrogen peroxide and the sodium, potassium and ammonium persulfates.

The alkali metal and ammonium persulfate catalysts may be employed by themselves or in activated redox systems. Typical redox systems include the persulfates in combination with: a reducing substance such as a polyhydroxy phenol and an oxidizable sulfur compound such as sodium sulfite or sodium bisulfite, a reducing sugar, a diazomercapto compound, a ferricyanide compound and dimethylaminopropionitrile. Heavy metal ions such as silver, cupric, iron, cobalt, nickel and others may also be used to activate persulfate catalyzed polymerizations. The well known redox systems using organic peroxides and organic hydroperoxides may also be used advantageously. In general the amount of free radical initiator employed will range between 0.1 to 5% based on the weight of the total monomers. The initiator is generally completely charged at the start of the polymerization, however, incremental addition or proportioning of the initiator throughout the polymerization is often desirable. In conducting the polymerization for the preparation of the latices - the possible starting materials of the present invention - the monomers are typically charged into the polymerization reactor which contains the water and the emulsifying agent. The reactor and its contents are then heated and the polymerization initiator added. The temperature at which the polymerization is conducted is not critical and may range from 0°C or lower to 85°C or higher. Excellent results, however, have been obtained when the polymerization temperature is maintained between 5°C and 60°C. Polymerization modifiers such as the pri-

mary, secondary, and tertiary mercaptans, buffers and electrolytes may also be included in the polymerization.

In the practice of the invention, when at least 90% of the monomers have copolymerized, more preferably after 93-95% monomers have been copolymerized, there is added to the polymerization mixture an amount of the comonomer being polymerized with acrylonitrile preferably in excess of the unpolymerized acrylonitrile, and additional catalyst, to induce copolymerization of said comonomer with the acrylonitrile effectively to decrease the amount of free residual acrylonitrile below 100 parts per million; more preferably below 25 parts per million. While the most effective comonomer amount that can be added may be used, there is a practical maximum amount in adding only a sufficient amount to insure reaction with substantially all of the free acrylonitrile to reduce the problem of loss or recovery of the excess comonomer. Normally an amount from equimolar to 50 mole percent excess to the acrylonitrile will be satisfactory.

The catalyst employed is preferably one that will complete the reaction in a matter of only a few hours. The redox catalysts are well known and may be used that involve the use of a combination reducing agent and peroxy catalyst, for example, heavy metal compounds such as ferrous iron or cobalt are generally effective with organic peroxides such as capryloyl peroxide, lauroyl peroxide, cumene hydroperoxide and diisopropyl benzene hydroperoxide. Also useful in such systems are polyhydroxy ketones such as the sugars with ferrous salts and cumene hydroperoxide. Gluconates have also been found to be useful. Other effective active catalyst systems include persulfate-bisulfite systems; peroxamine; sepamine and diazothioether catalyst systems, as are well known in the art, including those set forth hereinabove. Of course any catalyst system may be used, for example even sodium persulfate and hydrogen peroxide, but normally on a production basis it is desirable that equipment be tied up as short a period as possible for this step, so that the more active catalysts are employed to obtain faster reaction rates and equipment turn around. Other known catalysts such as potassium persulfate may be used if longer reactions are acceptable.

The acrylonitrile level may be decreased in accordance with the invention by adding the excess comonomer and catalyst in the reactor after 90% conversion has been reached, in blow-down, hold or storage tanks after removal from the polymerization reactor; or in any suitable container preferably equipped with agitation and heating means. In the selection of comonomer, it will be understood that in polymer dispersions of high conversion a different monomer may be introduced for reaction with the acrylonitrile in those situations where small amounts of another copolymer are not undesirable. For example, in the preparation of a copolymer of styrene and acryl-

onitrile where at the end of the polymerization there are present several thousand or more parts of unreacted acrylonitrile a redox catalyst and butadiene-1,3 may be added to the polymerization and the acrylonitrile removed by reaction with the butadiene and the small amount of copolymer thus formed would normally be mixed in with the copolymer of styrene and acrylonitrile in such amounts as to be not undesirable. Butadiene is a particularly useful monomer and would be used to reduced the acrylonitrile level of polymer dispersions since it reacts readily with acrylonitrile, particularly when present in an excess, and because of its low boiling point of about -4°C , it is easily and efficiently removed from the polymer dispersion without expensive or extensive processing.

As stated, any catalyst system effective in the copolymerization of acrylonitrile with other monomers at reasonable temperatures, in the range of

5 to 95°C , more preferably 20 to 50°C , may be used. When butadiene is used as the reactive comonomer for decreasing the level of acrylonitrile the amount present should be in excess; for example, the butadiene level should be greater than the combining ratio or combining weight of butadiene with acrylonitrile, which is 63 to 37. The amount of catalyst employed based on the peroxy compound, preferably is an amount at least about 0.10 part peroxy compound based on the total monomer and polymer present.

With effective redox type catalyst systems, a temperature range of 25 to 50°C is satisfactory to provide reaction rates of 3 to 5 hours with a resulting amount of residual acrylonitrile obtained of less than 100 ppm (mg/kg). In other words, reaction temperatures of room temperature to 60°C which are normal polymerization temperatures for the aqueous polymerization of acrylonitrile polymers are satisfactory.

Table I

Recipe	A	B	C	D	E	F
NaHCO_3	0.2	0.2	0.2	0.2	0.2	0.2
Butadiene-1,3	55	55	55	55	55	55
Acrylonitrile	45	45	45	45	45	45
Bisopropyl xanthogen disulfide	1.0	1.0	1.0	1.0	1.0	1.0
Water	150	150	150	150	150	150
Potassium soap of tallow acid	5.0	5.0	5.0	5.0	5.0	5.0
$\text{Na}_2\text{S}_2\text{O}_4$	0.04	0.04	0.04	0.04	0.04	0.04
$\text{K}_2\text{S}_2\text{O}_8$	0.3	0.3	0.3	0.03	0.3	0.3
Daxad 17 ¹⁾	1.0	1.0	1.0	1.0	1.0	1.0
Sequesterene NA3 ²⁾	0.03	0.03	0.03	0.03	0.03	0.03
Sodium hexahydroxyheptonate	0.02	0.02	0.02	0.02	0.02	0.02
Dimethylamine	0.02	0.02	0.02	0.02	0.02	0.02
Post polymerization addition						
Butadiene-1,3	0	0	6.0 g	10.0 g	6.0 g	11.5 g
Sequesterene NA3 ²⁾	0	0.001	0.001	0.001	0.001	0.001
Sequesterene NAF ³⁾	0	0.001	0.001	0.001	0.001	0.001
Sodium hexahydroxyheptonate	0	0.001	0.001	0.001	0.001	0.001
$\text{NA}_2\text{S}_2\text{O}_4$	0	0.15	0.15	0.15	0.15	0.15
Water	0	5.0	5.0	5.0	5.0	5.0
Diisopropylbenzene hydroperoxide	0	0.1	0.1	0.1	0.1	0.1
Results of post-polymerization additions						
First addition phm ⁴⁾						
Butadiene	None	None	6	11.5	6	11.5
SFS ⁵⁾	None	0.15	0.15	0.15	0.15	0.15
DIP ⁶⁾	None	0.1	0.1	0.1	0.1	0.1
Second addition, phm						
Butadiene	None	None	6	12	10.5	None
SFS ⁵⁾	None	0.15	0.15	0.15	—	—
DIP ⁶⁾	None	0.1	0.1	0.1	0	0
Residual acrylonitrile, mg/kg (ppm)	16,300	16,600	10	6	8	10

1) Sodium salt of condensed naphthalene sulfonate-formaldehyde

2) Trisodium ethylenediaminetetraacetate (Ciba-Geigy)

3) Sodium iron ethylenediaminetetraacetate (Ciba-Geigy)

4) phm — Parts per hundred of polymer

5) Sodium formaldehyde sulfoxylate

6) Diisopropylbenzene hydroperoxide

Example

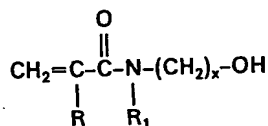
A copolymer of butadiene and acrylonitrile was prepared in water to form a latex in accordance with the recipe set forth in the Table below. With the exception of the control, additional butadiene and catalyst were added to the polymerization mixture after the monomers had reached a conversion to polymer of approximately 95%. All parts were parts by weight. The results in residual acrylonitrile after treatment were set forth in the Table. Run A was the control, with no addition of butadiene or catalyst. Run B demonstrates the ineffectiveness of catalyst alone without the comonomer. Raising the temperature of the control from the polymerization temperature of 35°C to 72°C for two hours did not result in any decrease in residual acrylonitrile. The temperature was also raised in Run B with no resultant decrease in acrylonitrile content after several hours at the elevated temperature. In Runs C and D a second butadiene and catalyst addition was made after the initial addition and as shown in Run F where no second addition was made, such second addition is normally not necessary.

On a production scale butadiene/acrylonitrile copolymer latex is prepared, which after conversion was essentially complete, contained about 8000 to 15000 ppm of free acrylonitrile. There was added to the latex 5 parts of water containing 0.001 phr of sodium hexahydroxyheptonate, 0.001 phr of sodium ferric ethylenediamine tetraacetic acid salt, 0.001 phr of trisodium ethylenediaminetetraacetic acid salt, 0.1 phr of sodium formaldehyde sulfoxylate, and 0.1 phr of sodium sulfite, 5 phr of butadiene-1,3 and 0.2 phr of cumene hydroperoxide (0.3 of 70% cumene hydroperoxide) at a temperature of about 35°C. After about 4 hours, the residual or free acrylonitrile had been reduced to an average of about 50 ppm.

When similar tests are conducted with latices containing for example, 20% total solids of a polymer of acrylonitrile containing unreacted acrylonitrile; an ABS latex containing free acrylonitrile; and an ethyl acrylate-acrylonitrile copolymer latex, treated respectively with additional styrene or butadiene-1,3, butadiene-1,3 or ethyl acrylate where appropriate, with a redox catalyst, the amount of free acrylonitrile is substantially reduced to less than 100 ppm.

Claims

1. A method for reducing the residual acrylonitrile dissolved in acrylonitrile homo- or copolymer and/or water by adding to the aqueous polymerization system, which has polymerized to a conversion of at least 90%, a copolymerizable monomer and copolymerizing acrylonitrile and said monomer, which method comprises adding to said emulsion a monomer selected from the group comprising vinyl aromatic monomers; alpha-olefins; alkyl vinyl ethers; vinyl ketones; acrylamides of the formula



wherein R and R₁ may independently be a C₁₋₄ alkyl radical or hydrogen; x is an integer from 1 to 4; methylene bis acrylamide; ethylene glycol dimethacrylate; diethylene glycol diacrylate; allyl pentaerythritol; divinyl benzene; butadiene; and a mixture thereof; in an amount at least equivalent to the residual acrylonitrile in said aqueous emulsion; and adding from about 0.1 to 5% by weight, based on the combined weight of residual acrylonitrile and added monomer, of a catalyst system comprising an organic peroxide or a hydroperoxide and a reducing agent comprising a heavy metal compound or a reducing sugar and maintaining the resulting composition at a temperature of from 5 to 95°C for a period of time to reduce the residual acrylonitrile content to less than 100 ppm.

2. A method according to Claim 1 wherein the monomer is added to said emulsion in an amount up to about a 50 molar % excess over the amount of residual acrylonitrile.

3. The method of Claim 2 wherein said acrylonitrile polymer is a copolymer of butadiene and acrylonitrile, said comonomer is butadiene and is added in an amount to provide a weight ratio of added butadiene to residual acrylonitrile which is greater than 63 to 37, said catalyst is a redox catalyst, and said conversion is greater than 93%.

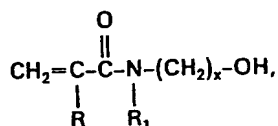
4. The method of Claim 3 wherein said redox catalyst consists of an organic peroxide and a reducing heavy metal compound.

5. The method of Claim 3 wherein the temperature of addition of butadiene and redox catalyst is between 25 to 60°C and the amount of residual free acrylonitrile resulting is less than 100 ppm.

6. The method of Claim 3 wherein the amount of butadiene and acrylonitrile initially copolymerized is from 60 to 80 weight percent butadiene-1,3 and 20 to 40 weight percent acrylonitrile.

Patentansprüche

1. Verfahren zur Verminderung des restlichen, in Acrylnitril-Homo- oder -Copolymer und/oder Wasser gelösten Acrylnitrils durch Zugabe eines copolymerisierbaren Monomers zu dem wässrigen Polymerisationssystem, in dem die Polymerisation bis zu einer Umwandlung von wenigstens 90% erfolgt ist, und Copolymerisieren des Acrylnitrils und des Monomers, umfassend die Zugabe eines Monomers ausgewählt aus der vinylaromatischen Monomere, alpha-Olefine, Alkylvinylether, Vinylketone, Acrylamide der Formel



in der R und R₁ unabhängig voneinander ein C₁₋₄-Rest oder Wasserstoff sein können und x eine ganze Zahl von 1 bis 4 ist, Methylenbisacrylamid, Ethylenglycoldimethacrylat, Diethylenglycoldiacrylat, Allylpentaerythrit, Divinylbenzol, Butadien und einem Gemisch derselben umfassenden Gruppe zu der Emulsion in einer Menge, die wenigstens dem restlichen Acrylnitril in der Emulsion äquivalent ist, und die Zugabe von etwa 0,1 bis 5 Gew.-%, bezogen auf das Gesamtgewicht aus dem restlichen Acrylnitril und dem zugesetzten Monomer, eines Katalysatorsystems, das ein organisches Peroxid oder ein Hydroperoxid und ein eine Schwermetall-Verbindung oder einen reduzierenden Zucker umfassendes Reduktionsmittel umfasst, und das Halten der resultierenden Zusammensetzung bei einer Temperatur von 5°C bis 95°C während einer Zeitspanne, um den Gehalt an restlichem Acrylnitril auf weniger als 100 ppm zu reduzieren.

2. Verfahren nach Anspruch 1, worin das Monomer der Emulsion in einer Menge bis zu einem molaren Überschuss von etwa 50% über die Menge des restlichen Acrylnitrils zugesetzt wird.

3. Verfahren nach Anspruch 2, worin das Acrylnitril-Polymer ein Copolymer aus Butadien und Acrylnitril ist, das Comonomer Butadien ist und in einer solchen Menge zugesetzt wird, dass das Gewichtsverhältnis des zugesetzten Butadiens zu dem restlichen Acrylnitril grösser als 63 zu 37 ist, der Katalysator ein Redox-Katalysator ist und die Umwandlung grösser als 93% ist.

4. Verfahren nach Anspruch 3, worin der Redox-Katalysator aus einem organischen Peroxid und einer reduzierenden Schwermetall-Verbindung besteht.

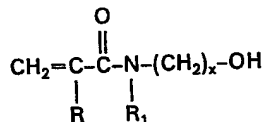
5. Verfahren nach Anspruch 3, worin die Temperatur der Zugabe des Butadiens und des Redox-Katalysators zwischen 25°C und 60°C liegt und die Menge des resultierenden restlichen freien Acrylnitrils kleiner als 100 ppm ist.

6. Verfahren nach Anspruch 3, worin die Menge des anfangs copolymerisierten Butadiens und Acrylnitrils 60 bis 80 Gew.-% Butadien-1,3 und 20 bis 40 Gew.-% Acrylnitril betragen.

Revendications

1. Procédé pour réduire la quantité d'acrylonitrile résiduel dissoute dans un homopolymère ou un copolymère d'acrylonitrile et/ou dans l'eau par addition au système aqueux de polymérisation, qui a été polymérisé jusqu'à un degré de transformation d'au moins 90%, d'un monomère copolymérisable, et copolymérisation de l'acrylonitrile et dudit monomère, procédé qui consis-

te à ajouter à ladite émulsion un monomère choisi dans le groupe comprenant des monomères vinyliques aromatiques; des alpha-oléfiniques; des éthers d'alkyle et de vinyle; des vinylicétones; des acrylamides de formule



dans laquelle R et R₁, indiqués ci-dessous, peuvent représenter un radical alkyle en C₁ à C₄ ou l'hydrogène; x est un nombre entier de 1 à 4; du méthylène-bis-acrylamide; du diméthacrylate d'éthylène glycol; du diacrylate de diéthylène glycol; de l'allylpentaérythritol; du divinylbenzène; du butadiène; et leurs mélanges; en une quantité au moins équivalente à l'acrylonitrile résiduel présent dans ladite émulsion aqueuse; et à ajouter environ 0,1 à 5% en poids, sur la base du poids total d'acrylonitrile et de monomère ajouté, d'un système catalyseur comprenant un peroxyde organique ou un hydroperoxyde et un agent réducteur comprenant un composé de métal lourd ou un sucre réducteur et à maintenir la composition résultante à une température de 5 à 95°C pendant une période suffisante pour réduire à moins de 100 ppm la teneur en acrylonitrile résiduel.

2. Procédé suivant la revendication 1, dans lequel le monomère est ajouté à ladite émulsion en une quantité allant jusqu'à un excès molaire d'environ 50% par rapport à la quantité d'acrylonitrile résiduel.

3. Procédé suivant la revendication 2, dans lequel le polymère d'acrylonitrile est un copolymère de butadiène et d'acrylonitrile, le comonomère est le butadiène et est ajouté en une quantité donnant un rapport en poids du butadiène ajouté à l'acrylonitrile résiduel qui est supérieur à 63:37, le catalyseur est un catalyseur d'oxydo-réduction et le taux de transformation est supérieur à 93%.

4. Procédé suivant la revendication 3, dans lequel le catalyseur d'oxydo-réduction est constitué d'un peroxyde organique et d'un composé de métal lourd réducteur.

5. Procédé suivant la revendication 3, dans lequel la température d'addition du butadiène et du catalyseur d'oxydo-réduction se situe entre 25 et 60°C et la quantité d'acrylonitrile résiduel libre résultant est inférieure à 100 ppm.

6. Procédé suivant la revendication 3, dans lequel la quantité de butadiène et d'acrylonitrile initialement copolymérisée va de 60 à 80% en poids de butadiène-1,3 et de 20 à 40% en poids d'acrylonitrile.